Organic Compounds of Arsenic, Part VI : Electrolytic Reduction of Some Aryl-Arsinic Acids

AUTHOR(S):

Matsumiya, Kaoru; Nakata, Hisakazu

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By

Kaoru Matsumiya and **Hisakazu Nakata**

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In our previous work[1] on the electrolytic reduction of 3-nitro-4-hydroxyphenylarsinic acid, it was shown that the cathode material and the strength of the acid in the cathode solution have remarkable effects on the final products of electrolysis. The cathode materials used were then limited to mercury, lead and lead amalgam; we have therefore continued the work further to see the effects of platinum, nickel and copper when used as the cathode.

It is already known that arsenic and arsinic acids are not reduced in an alkaline medium[2]. In an acidic medium, however, it was found, as stated below, that arsinic acid radical is also practically not reducible when cathodes of lower over-voltage are used. In fact, with the cathode of platinum, nickel or copper, the reduction of 3-nitro-4-hydroxyphenylarsinic acid takes place only in the nitro group, there being formed 3-amino-4-hydroxyphenylarsinic acid and 3,3′-azoxy-4,4′-dihydroxyphenyl-1,1′-diarsinic acid. Similarly, 3,4-diaminophenylarsinic acid is obtained as the reduction product from 3-nitro-4-aminophenylarsinic acid.

The concentration of the acid exerts on the reduction of 3-nitro-4-hydroxyphenylarsinic acid[3] such an influence that in a dilute hydrochloric acid solution it goes on directly to the arsine stage, while at a higher concentration it remains only in the state of the arseno-compound. To

1 *These memoirs*, **10**, 199 (1926)
2 Covelli: Chem. Ztg., **33**, 1209 (1909);
F. Fichter and E. Elkind: Ber., **49** 239 (1916)
3 Our previous paper, loc. cit.

see whether the same influence is observed with the other arsinic acids, experiments were undertaken with 4-aminophenylarsinic acid and 4-hydroxyphenylarsinic acid.

According to Fr. Fichter and E. Elkind[1] 4-aminophenylarsinic acid is reduced to 4-aminophenylarsine with dilute hydrochloric acid, but with the acid more concentrated than 2-N, the hydrochloride of 4-aminophenylarsine, which is insolube in concentrated hydrochloric acid, covers the surface of the cathode and hinders the further progress of reduction. In our experiments with 4-aminophenylarsinic acid in concentrated hydrochloric acid solution a similar result to that in the case of 3-nitro-4-hydroxyphenylarsinic acid was obtained, p-arsenoaniline being its reduction product. We could also prepare 4-hydroxyphenylarsine and 4,4′-dihydroxyarsenobenzene from 4-hydroxyphenylarsinic acid in a similar manner by changing the acidity of the catholyte.

The limit of concentration of the acid beyond which the reduction product changes from arsine to arsenocompound is not always the same; it is 4.7-N for 3-amino-4-hydroxyphenylarsine and 3,3′-diamino-4,4′-dihydroxyarsenobenzene, 8-N for 4-aminophenylarsine and 4,4′-diaminoarsenobenzene, and 4-N for 4-hydroxyphenylarsine and 4,4′-dihydroxyarsenobenzene. Perhaps this property may be utilized as a convenient, electrolytical method for preparing various arseno-compounds from the corresponding arsinic acids.

Experimental Part

1) Reduction of 3-nitro-4-hydroxyphenylarsinic acid with platinum, nickel and copper cathodes

A patent process[2] is known for preparing aminoxyphenylarsinic acid by electrolyzing 3-nitro-4-hydroxyphenylarsinic acid in an alkaline solution. We have, however, found that an acid solution may also be used for the same purpose in the following manner :—

The cathode solution was prepared by dissolving 2 grms. of 3-nitro-4-hydroxyphenylarsinic acid in 125 c.c. of 2.5-N HCl and into this solution a platinum plate (4 × 10 cm.) was dipped as cathode. When a current of 2 amps. was passed at 25°, the cathode solution soon became brown and

1 loc. cit.

2 U. S. P., 1232373

the yellow precipitate of azoxyphenoldiarsinic acid began to separate. The solution was vigorously stirred during the electrolysis in order to prevent the cathode from being covered with the precipitate. After 80 minutes the current was cut off; the yellow precipitate was separated by filtering and dried in a desiccator. To the filtrate 45 grms. of sodium acetate was added, by which 3-amino-4-hydroxyphenylarsinic acid was separated in a brown crude state.

3,3′-azoxy-4,4′-dihydroxyphenyl-1, 1′-diarsinic acid is a yellow, fine needle crystal which darkens at about 210° and gradually decomposes without melting. It is soluble in hot water, methyl and ethyl alcohol; sparingly so in cold water and dilute mineral acids; and insoluble in acetone, ether, benzene, chloroform and carbon bisulphide. Its aqueous solution has an acid reaction on litmus. When treated with zinc dust, its alkaline solution becomes by and by colourless, and this colourless solution shows a power of reducing ammoniacal silver nitrate, while the original acid does not.

It was recrystallized from hot water and analysed with the following result:—

0.0988 grms. subst. required 15.20 c.c. of N/10 iodine soln.

0.1313 grms. subst. gave 0.1450 grms. CO_2 and 0.0327 grms. H_2O.

	found	calc. for $C_{12}H_{12}O_5N_2As_2$
C	30.13%	30.14%
H	2.78%	2.53%
As	31.31%	31.36%

To purify the crude aminoxyphenylarsinic acid obtained by the above method, it was dissolved in dil. HCl, decolourized with animal charcoal and recrystallized from a solution containing sodium acetate. It darkens at 170° and decomposes gradually. Its dil. HCl-solution assumes a deep red colour on the addition of one drop of potassium bichromate solution, which is the characteristic property of the aminoxyphenylarsinic acid.

0.1860 grms. subst. required 15.20 c.c. of N/10 iodine soln.

	found	calc. for $C_6H_8O_4NAs.\frac{1}{2}H_2O$
As	30.65%	30.97%

The acid acetylated with acetic anhydride was also analysed.

0.1665 grms. subst. required 12.00 c.c. of N/10 iodine soln.

	found	calc. for $C_8H_{10}O_5NAs$
As	27.03%	27.25%

When working with a nickel or a copper cathode, we could also observe the presence of a compound other than the above-mentioned,

though it could not be isolated on account of its being too small in quantity. From the properties of the compound in solution, however, it may certainly be inferred that the arsinic acid radical must have undergone reduction.

The relation between the amounts of the reduction-products and cathode material is as follows :—

Anode :	carbon
Catholyte :	2 grms. 3-nitro-4-hydroxyphenylarsinic acid in 125 c.c. 2.5-N HCl
Anolyte :	2.5-N HCl
Current :	2 amps.
Time :	1 1/3 hours.
Temperature :	25°

Cathode (4×10 sq. cm.)	Azoxyphenoldiarsinic acid (grm.)	Aminoxyphenylarsinic acid (grm.)
copper	0.25	1.05
nickel	0.46	0.72
platinum	0.70	0.62

2) Reduction of 3-nitro-4-aminophenylarsinic acid with copper cathode

The cathode solution was prepared by dissolving 5 grms. of 3-nitro-4-aminophenylarsinic acid in a mixture of 30 c.c. of HCl (D. 1.19), 90 c.c. of methyl alcohol and 10 c.c. of water. Taking a copper plate (5×10 cm.) as the cathode, a current of 1 amp. was passed at 28–30° for 6 hours, the cathode solution becoming brownish during the electrolysis. After evaporating methyl alcohol at a reduced pressure the cathode solution was carefully neutralized with sodium hydroxide, when 3, 4-diaminophenylarsinic acid separated out as chocolate-brown crystals. It was decolourised with animal charcoal and recrystallized from hot water. It crystallizes in colourless, minute needles which darken at 140° and melt, with decomposition, at 158°. Its dil. HCl-solution produces a deep violet colour with potassium bichromate solution. The yield was about 70 per cent.

0.1630 grms. subst. required 13.45 c.c. of N/10 iodine soln.

	found	calc. for $C_6H_3O_3N_2As.\frac{1}{2}H_2O$
As	30.95%	31.09%

3) Reduction of 4-aminophenylarsinic acid.

a) Preparation of p-arsenoaniline

The apparatus was the same as shown in the previous paper[1]; all the experiments were carried in a carbon dioxide atmosphere.

Five grms. of 4-aminophenylarsinic acid dissolved in 50 c.c. of 11-N HCl were reduced at the mercury cathode (28 sq. cm.) by a current of 1 amp., the temperature being kept at 25°. After the electrolysis the yellow precipitate of 4,4′-arsenoaniline dihydrochloride was separated by filtration and dried in vacuo over sodium hydroxide. The yield was 55 per cent.

0.2185 grms. subst. required 20.48 c.c. of N/10 iodine soln.

	found	calc. for $C_{12}H_{14}N_2As_2Cl_2.H_2O$.
As	35.18%	35.27%

b) Influence of the strength of acid

Cathode: mercury
Anode: carbon
Catholyte; 3 grms. 4-aminophenylarsinic acid in 60 c.c. of HCl
Anolyte: HCl of the same strength as the catholyte
Current: 1 amp.
Temperature: 25–30°

Normality of acid	Aminophenylarsine hydrochloride (grm.)	Arsenoaniline dihydrochloride (grm.)
3	2.1	0
6	1.7	0
8	0.1	0.6
10	0	1.2

1 loc. cit.

4) Reduction of 4-hydroxyphenylarsinic acid

a) Preparation of 4-hydroxyphenylarsine

Four grms. of 4-hydroxyphenylarsinic acid dissolved in 100 c.c. of 1-N HCl were reduced by means of a mercury cathode with a current of 1 amp. the temperature being kept at 25–30°. After electrolysis for 5 hours the whole cathode solution, which contained some yellowish precipitates, was made alkaline with sodium hydroxide, through which carbon dioxide gas was passed, whereupon slightly yellow coloured needle crystals of 4-hydroxyphenylarsine separated out. It was filtered and dried; the yield was 48 per cent. It becomes reddish at 75° and decomposes completely at 155°.

0.1446 grms. subst. required 16.80 c.c. of N/10 iodine soln.

	found	calc. for C_6H_7OAs
As	43.57%	44.07%

b) Preparation of p-arsenophenol

The cathode solution was prepared by disssolving 5 grms. of 4-hydroxyphenylarsinic acid in 100 c.c. of 6-N HCl and was subjected to electrolytic reduction under conditions similar to those in the previous experiment. After 4 hours the current was cut off and the brown precipitate of p-arsenophenol was separated. It was purified by reprecipitation with carbon dioxide gas from its alkaline solution. The yield was 60 per cent. It is a yellowish brown powder which darkens and decomposes at 200°.

0.1321 grms. subst. required 15.80 c.c. of N/10 iodine soln.

	found	calc. for $C_{12}H_{10}O_2As_2$
As	44.85%	44.61%

The Institute for Chemical Research,
Imperial University of Kioto.